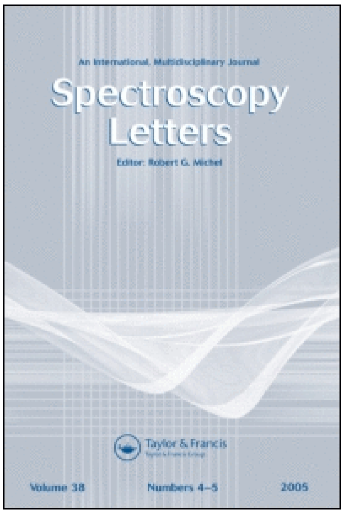

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A NEW SIMULTANEOUS SPECTROPHOTOMETRIC METHOD FOR DETERMINATION OF IRON(II) AND IRON(III) IN NATURAL WATERS

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A NEW SIMULTANEOUS SPECTROPHOTOMETRIC METHOD FOR DETERMINATION OF IRON(II) AND IRON(III) IN NATURAL WATERS

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ABSTRACT

A new analytical method employing di-2-pyridyl ketone salicyloylhydrazone (DPKSH) as a colorimetric chelating agent for simultaneous spectrophotometric determination of iron(II) and iron(III) in natural waters has been developed. Both of the complex ions show an absorbance maximum at 375 nm, with 4.21×10^4 and $1.26 \times 10^4\,l \cdot mol^{-1} \cdot cm^{-1}$ as the molar absorptivities, respectively, for Fe(II) and Fe(III). DPKSH complexes with Fe(II) show another absorbance maximum at 644 nm and a molar absorptivity equal to $1.27 \times 10^4\ l \cdot mol^{-1} \cdot cm^{-1}$. The detection limits are 0.09 μM for Fe(II) and 0.22 μM for Fe(II + III). Concentration approaches were done by using data from five analytical curves for Fe(II), Fe(III) and Fe(II + III) solutions and the use of the respective equations was evaluated in respect on the accurity. Analytical interference studies on some ions probably found in natural waters have also been

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carried out. This analytical method was used to determine Fe(II) and Fe(III) in natural waters and compared to the 2,2′-bipyridyl and Atomic Absorption spectroscopy methods.

Key Words: Iron; Hydrazones; DPKSH; Natural waters.

INTRODUCTION

Iron is one of the major inorganic components of the Earth, being present in rocks and soil minerals in the average concentration of 5.6% (1). Although liquid water is a minor component of the troposphere, the chemical reactions that occur in the water droplets (clouds, fog or rain) affect the composition of the atmospheric input to terrestrial and aquatic ecosystems. Iron(II) and (III) are involved in many of these processes particularly in redox and radical chain reactions (2).

In the urban atmosphere S(IV), like SO_2. organic components, Fe(II and III), Mn(II), Cu(II), Pb(II) and oxidants like O_2, O_3, H_2O_2, $OH^\bullet$ can be present (3). Sulphur(IV) is a very important natural and anthropogenic pollutant in the atmosphere (4). because of its relative large abundance. Iron(III) is one of the most active catalyst of the autoxidation of S(IV) to S(VI) (5,6) and this oxidation state change is very important since sulphate is the most important component of acid rain (7). Iron is unquestionably the most important bioactive trace metal in the oceans because it is an essential micronutrient for phytoplankton growth (8,9). In addition, iron plays an important role in the biosphere being an active center of proteines such as oxidases, reductases and dehydrases (10). For all of these reasons the determination of the oxidation state of iron in atmospheric water is very important.

A variety of methods have been developed to determine iron. However most of them cannot determine iron(II) and (III) simultaneously. They have been limited to the determination of total iron (11) or only iron(II) (12) and (III) separately (13). Complexometric methods followed by spectrophotometric measurements are generally used for determination of iron in samples (14–17). Di-2-pyridyl ketone benzoylhydrazone (DPKBH) was used to determine the amount of Fe(II) and Fe(III) in synthetic solutions ($pH = 5.0$) and cloud water (pH 6.5), respectively, by Zatar et al. (18) and Pehkonen et al. (14) in ethanol-water medium 50%. In these conditions it is known that the reaction between Fe(III) and S(IV) is very fast and the composition of the samples is quickly changed (19). In spite of this, use of such a ligand is very interesting because it forms complexes simultaneously with both species showing absorbance maxima at 370 for Fe(II) and Fe(III) and at 660-nm only for Fe(II).

However, a contradictory fact in respect on the DPKBH reagent is that Zatar et al. (18) and Pehkonen et al. (14) found a similar behavior for Fe(II) and Fe(III) at almost the same wavelength but Garcia-Vargas et al. (20) found very different values of molar absorptivities. In benzene and pH 5, other contradiction is found for Fe(II) and Fe(III) complexes with DPKBH. Garcia-Vargas et al. (20) found different molar absorptivities for Fe(II) ($4.4 \times 10^4\ \mathrm{l \cdot mol^{-1} \cdot cm^{-1}}$) and Fe(III) ($6.1 \times 10^3\ \mathrm{l \cdot mol^{-1} \cdot cm^{-1}}$), at 380 nm, and Nakanishi and Otomo (21) did not observe the reaction between Fe(III) and DPKBH. Suárez-Iha et al. (22) have determined the stoichiometric, structure and thermodynamics of the Fe(II) and Fe(III) complexes with DPKBH confirming the quite favorable coordination of both of the ions with this reagent.

In a review Pehkonen (23) has presented several methods to determine Fe(II) and Fe(III) emphasizing the importance of the potential changes in the oxidation state of iron in natural water samples when a chelating agent is added and he has focused the problems associated with these changes.

In order to minimize some interferences found in several methods for iron determination another method using a different ligand, di-2-pyridyl ketone salyciloylhydrazone (DPKSH), was developed. This ligand complexes with both species and shows absorbance maxima at 375 for Fe(II) and Fe(III) and at 644 nm only for Fe(II) and it seems to be a better reagent than DPKBH because it forms stable complexes with Fe(II) and Fe(III) at lower pH values which are common in some natural waters.

EXPERIMENTAL

Reagents and Solutions

Iron(II) and iron(III) stock solutions were prepared by dissolving, respectively, the salts ammonium iron(II) sulfate and iron(III) perchlorate. The pH was adjusted to 1.0 with perchloric acid and the respective concentration of Fe(II) and Fe(III) was determined by titration with EDTA and variamine Blue as indicator (24).

Chloroacetic acid - chloroacetate mixtures (mol/l) were used to keep the pH equal to 2.2 (2.4/0.14), 3.0 (0.37/0.45) and 3.4 (0.14/0.48). For pH 4.1 (4.1/1.0) and 5.0 (0.7/1.0) acetic acid - acetate buffer solutions (mol/l) were used.

A freshly aqueous solution of 2,2′-bipyridyl (BIPY) 0.1% was prepared to apply the comparative method (25). The reduction of Fe(III) to Fe(II) was carried out with ascorbic acid.

The water samples named A, B, C and D were collected in aquifers from different locations at the south of Minas Gerais in Alfenas city, which is surrounded by the Furnas water power plant. After the collection, the samples were filtered in Whatman 43 filter paper and stored in polyethylene bottles. The pH of the samples was adjusted to 1.0 with perchloric acid and the bottles were kept at 5°C in a refrigerator.

The synthesis of di-2-pyridyl ketone salicyloylhydrazone (DPKSH) was performed according to the procedure outlined by Garcia-Vargas et al. (20) involving the reaction between di-2-pyridyl ketone and salicyloylhydrazide reagents in equimolar amounts. The solid product was recrystallized twice from an ethanol-water solution. After synthesis, the melting point of the product (179–181°C), the elemental analysis and the infrared spectrum obtained using a potassium bromide disk, were determined and all of the results were in excellent agreement with the data from the literature (20).

RESULTS AND DISCUSSION

Spectral Characteristics of DPKSH and Its Complexes with Iron(II) and (III)

The DPKSH has a low solubility in ethanol (20) and has a much lower solubility in water. Using different ethanol percentages in the range of 10 to 50 the spectra of solutions containing Fe(II) = 15.3 μM, DPKSH = 2.40 mM and pH = 3.0 (adjusted with chloroacetate buffer) were registered. The highest absorbance value was attained at 50%(v/v) of ethanol/water solution. This condition was used in all steps of the work.

In ethanol 50%(v/v) the spectrum of DPKSH ligand shows significant absorbance in the UV region and a maximum absorbance at 320 nm while Fe(II) complex shows two bands with maxima at 375 and 644 nm; $4.21 \times 10^4\,\mathrm{l \cdot mol^{-1} \cdot cm^{-1}}$ and $1.27 \times 10^4\,\mathrm{l \cdot mol^{-1} \cdot cm^{-1}}$ are the molar absorptivities, respectively. The complexes with Fe(III) shows only one maximum absorbance at 375 nm and a molar absorptivity of $1.26 \times 10^4\,\mathrm{l \cdot mol^{-1} \cdot cm^{-1}}$. Figure 1 shows the spectra of the ligand and its coordination compounds with Fe(II) and Fe(III).

Optimization of the Analytical Parameters

The pH influence in the iron(II) and iron(III) complexation with DPKSH was checked for pH values of 2.2; 3.0; 3.4; 4.1 and 5.0 in ethanol/water 50%(v/v). In the case of the Fe(II)/DPKSH system, the absorbance values at 644 nm became constant at pH $\geq$ 3.4. However, for the Fe(III)/DPKSH system that condition was only obeyed at pH $\geq$ 4.1. At pH below 4.1 a significant increase in the absorbance at 375 nm was observed probably due to the Fe(III) reduction.

Different ligand/metal ratios were used to establish the highest sensitivity. Iron(II) [20.0 μM] and Iron(III) [63.6 μM] solutions were prepared with

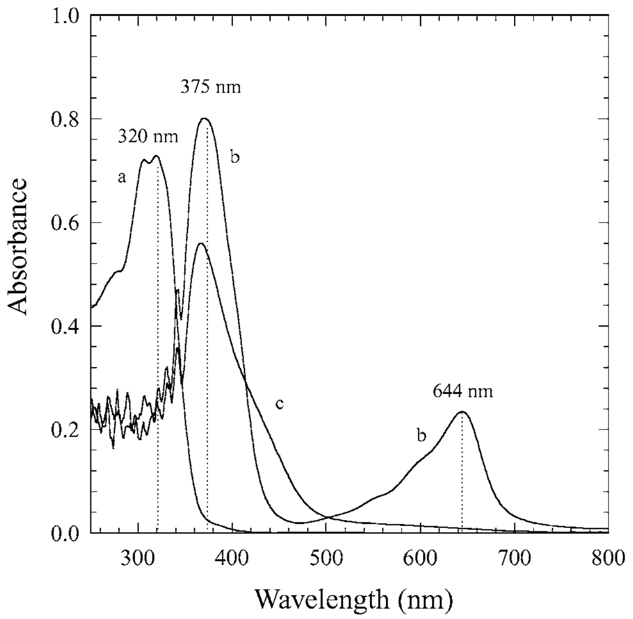

Figure 1. Spectra of DPKSH ligand and DPKSH/Fe^{n+} complexes in ethanol-water 50% v/v, pH = 4.1 and using a 1-cm optical cell. (a) $C_{DPKSH} = 50\,\mu M$; (b) $C_{Fe(II)} = 20.3\,\mu M$; $C_{DPKSH} = 240\,\mu M$; (c) $C_{Fe(III)} = 41.1\,\mu M$; $C_{DPKSH} = 424\,\mu M$.

ethanol/water 50%(v/v), pH 4.1 and several concentrations of DPKBH. The maximum absorbance for both of the systems was reached when the ligand/metal ratios are ≥ 10.

The reagent addition order is essential in some methods. Twelve reagent addition orders were checked and the best order for iron(II) and iron(III) was Fe, DPKSH, ethanol and buffer. Using this addition order the complexes and the color intensity remained constant for at least 2 h.

Effect of Foreign Ions

Experiments were carried out to check the effect of foreign ions in the determination of 10.2 and 21.2 μM of iron(II) and iron(III), respectively. The cations were added in the form of chlorides, nitrates and sulfates and anions in the form of sodium or potassium salts. The results are presented in Table1.

A positive interference was observed from the most of the ions except F^-, HPO_4^{2-}, oxalate, CO_3^{2-}, acetate, HCO_3^-, NO_2^-, AsO_2^-, propionate that caused

Table 1. Effect of Foreign Ions on Determination of Fe(II) and Fe(III)/DPKSH Complexes in Ethanol 50% (v/v) and $pH = 4.1$, $\lambda = 375$ nm: (a) $C_{Fe(II)} = 10.2\ \mu M$ and $C_{DPKSH} = 240\ \mu M$; (b) $C_{Fe(III)} = 21.2\ \mu M$, and $C_{DPKSH} = 424\ \mu M$

Tolerance Limit	(a) Fe(II)	(b) Fe(III)
≥10.000	Na^+, Cl^-, NO_3^-, K^+, F^-, SCN^-, $Ac^{-(a)}$, I^-	Na^+, K^+, Br^-
≥1000	Ca^{2+}, Ba^{2+}, $Prop^{-(b)}$, NH_4^+	Cl^-, $NO3^-$, Ba^{2+} , NH_4^+
≥100	Mg^{2+}, Al^{3+}, SO_4^{2-}, HPO_4^{2-}, HCO_3^-, NO_2^-, AsO_2^-, $For^{-(c)}$	Mg^{2+}, Ca^{2+}, SO_4^{2-}, SCN^-, $Ac^{-(a)}$, NO_2^-, I^-, $For^{-(c)}$, $Prop^{-(b)}$
≥10	Mn^{2+}, $Ox^{2-(d)}$, CO_3^{2-}, SO_3^{2-}	Al^{3+}, HPO_4^{2-}, $Ox^{2-(d)}$, CO_3^{2-}, HCO_3^-, F^-, AsO_2^-
≥1	Co^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Hg^{2+}, Ni^{2+}	Co^{2+}, Cd^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, Pb^{2+}, Hg^{2+}, Ni^{2+}, SO_3^{2-}

[a] Acetate, [b] propionate, [c] formate, and [d] oxalate.

a negative interference. However, the presence of these anions in a water sample must not be considered as a real interference to the method, they can be seen as controllers of the Fe(III) free concentration to be complexed with DPKSH. Real interferents to the Fe(III) determination are some metallic ions that are also coordinated by DPKSH absorbing at 375 nm. However, at 644 nm there is no interference from these ions making possible the exact determination of Fe(II).

Total iron concentration can be determined after the reduction of Fe(III) to Fe(II) with ascorbic acid and measuring the absorbance at 644 nm. Consequently, the Fe(III) concentration measurements can be achieved. For many atmospheric, groundwater and surface water samples this interference is not significant because the interfering metallic ion concentrations are generally found to be less than 5% of the iron concentration and the direct determination of Fe(II) and Fe(III) can be done without the reduction step (26).

Analytical Curves

The behavior of the Fe(II), Fe(III) and Fe(II + III) complexes with DPKSH was characterized from different experimental analytical curves. Absorbance measurements were carried out for solutions in ethanol 50%, pH 4.1, containing only Fe(II) (375 and 644 nm), only Fe(III) (375 nm) and the mixtures of Fe(II and III) (375 and 644 nm). Five analytical curves were constructed and the respective linear relationships were calculated from a minimum square mathematics treatment. The results are shown in Table 2.

The detection limit was defined as three times the standard deviation (SD) of the reagent blank reading at both wavelengths. The spectrophotometric detection

Table 2. Parameters Obtained from the Analytical Curves for Fe(II), Fe(III), and Fe(II + III), and Some Inherent Observations. n Is the Number of the Respective Equation

Species	Equation	n	Observations
Fe(II)	$\overset{375}{A}_{Fe(II)} = -(9.64 \pm 4.99) \times 10^{-3} + (4.21 \pm 0.04) \times 10^4.C_{Fe(II)}$	1	Fe (II) solution
	$\overset{644}{A}_{Fe(II)} = (4.18 \pm 3.58) \times 10^{-3} + (1.25 \pm 0.01) \times 10^4 C_{Fe(II)}$	2	Fe (II) solution
	$\overset{644}{A}_{Fe(II)} = (2.77 \pm 1.05) \times 10^{-3} + (1.27 \pm 0.01) \times 10^4 C_{Fe(II)}$	3	Fe(II+III) mixture
Fe(III)	$\overset{375}{A}_{Fe(III)} = -(1.06 \pm 1.05) \times 10^{-3} + (1.26 \pm 0.01) \times 10^4 C_{Fe(III)}$	4	Fe (III) solution
	$\overset{375}{A}_{Fe(II+III)} = (4.21 \pm 0.04) \times 10^4 CFe(II) + (1.26 \pm 0.01) \times 10^4 C_{Fe(III)}$	5	Fe(II+III) mixture Addition absorbance property
Fe(II+III)	$\overset{375}{A}_{Fe(II+III)} = -(6.21 \pm 2.94) \times 10^{-3} + (3.14 \pm 0.02) \times 10^4 C_{Fe(II+III)}$	6	Fe(II+III) mixture

limits are 0.15 μM (375 nm) and 0.09 μM(644 nm) for Fe(II) with a linear response from 0.5 up to 26 μM at 375 nm and 0.5 to 81 μM at 644 nm. The detection limit for Fe(III) is 0.2 μM at 375 nm with a linear response from 0.5 to up 73 μM.

As can be observed from Table 2, Equations 2 and 3, the slopes (molar absorptivities) are quite similar for the complexes of Fe(II) when the absorbances are measured for solutions with only Fe(II) or Fe(II) in presence of Fe(III). The molar absorptivities for complexes of Fe(II) and Fe(III) are quite different at 375 nm (Equations 1 and 4) and both of them are different from the slope of the Equation 6, obtained with the absorbances of the Fe(II + III) solutions. The absorbance of the last kind of solution can be written as the Equation 5 which represents the addition absorbance property that can be applied when there is no interaction among the species present in the solution.

The absorbance of a mixture at 644 nm is free of any interference and can be used to calculate the concentration of Fe(II) in a sample. But, at 375 nm, the quite different molar absorptivities of Fe(II) and Fe(III) complexes lead to different contributions to the measured absorbance. These different contributions were checked carrying out the absorbance measurements for the twenty-one different solutions of Fe(II) + Fe(III) coordinated to DPKSH, in ethanol 50% at pH 4.1.

Table 3. Criteria to Calculate Fe(II) and Fe(III) Concentrations

A^{375}/A^{644}	Fe(III)/Fe(II)	Procedure/Observations	
3.3	≤ 0.15	$A^{644}_{Fe(II)} = 2.77 \times 10^{-3} + 1.27 \times 10^{4} \cdot C_{Fe(II)}$ $A^{375}_{Fe(II+III)} = 4.21 \times 10^{4} \cdot C_{Fe(II)} + 1.26 \times 10^{4} \cdot C_{Fe(III)}$ Very low or negligible Fe(III) concentration	(3) (5)
Any value	0.15–0.9	$A^{644}_{Fe(II)} = 2.77 \times 10^{-3} + 1.27 \times 10^{4} \cdot C_{Fe(II)}$ $A^{375}_{Fe(II+III)} = -6.21 \times 10^{-3} + 3.14 \times 10^{4} \cdot C_{Fe(II+III)}$ $C_{Fe(III)} = C_{Fe(II+III)} - C_{Fe(II)}$	(3) (6)
Any value	>0.9	$A^{644}_{Fe(II)} = 2.77 \times 10^{-3} + 1.27 \times 10^{4} \cdot C_{Fe(II)}$ $A^{375}_{Fe(II+III)} = 4.21 \times 10^{4}\ C_{Fe(II)} + 1.26 \times 10^{4} \cdot C_{Fe(III)}$	(3) (5)

Table 3 summarize the three possible procedures to calculate the Fe(II) and Fe(III) concentrations, from the absorbances at 375 and 644 nm, for different solutions. If the A^{375}/A^{644} ratio is 3.3 Fe(III) /Fe(II) ratio obtained from Equation 5 defines the best way to calculate the Fe(III) concentrations: Equation 5 must be used if the ratio is <0.15; for ratios ≥ 0.15 Equation 6 is the best to use leading to the Fe(II + III) and, consequently, the Fe(III) concentration.

When the A^{375}/A^{644} is different from 3.3 two groups can be organized. The first one with Fe(III)/Fe(II) ratio >0.9 must be treated using Equation 5 (addition absorbance property); for the second one with $0.15 <$ Fe(III)/Fe(II) < 0.9 Equation 6 must be used. It is essential that, for both of the groups, the Fe(III)/Fe(II) ratio be obtained with the concentrations calculated using Equation 5.

The precision of the method was estimated for ten freshly prepared solutions containing 9.2 μM (5.1 μg) of iron(II) and 22.2 μM (12.4 μg) of iron(III). The absorbance measurements were carried out at 644 nm for Fe(II) and at 375 nm for total Fe. As the ratios of Fe(III)/Fe(II) concentrations are higher than 0.9, for any A^{375}/A^{644}, the more exact results were obtained using Equations 3 and 5. The relative standard deviations were 2 and 3%, respectively for Fe(II) and Fe(III).

Recommended Procedure for Determination of Iron(II) and Iron(III)

Aliquots of each stock solution of iron(II) and iron(III), 2 mL of 12 mM DPKSH ethanolic solution, 3 mL of ethanol, 150 μL of buffer solution at pH 4.1

are transferred to a 10 mL volumetric flask. Distilled water is added to complete the volume. After this an aliquot is transferred to a spectrophotometer cell and the absorbance is measured at 375 and 644 nm for total iron and iron(II), respectively.

Determination of Iron(II) and Iron(III) in Natural Waters

The accuracy of the recommended spectrophotometric procedure was evaluated by determining iron(II) and iron(III) in four natural water samples (A, B, C and D). The results were compared with the 2,2′-bipyridyl (BIPY) standard spectrophotometric method (25) and Atomic Absorption spectrometry; all results are presented in Table 4.

Both of the spectrophotometric (DPKSH and BIPY) methods showed an excellent agreement for Fe(II) in all the samples. The concentrations for samples A and C showed an agreement within 12 and –0.3%, respectively, and for samples B and D no Fe(II) was detected. The determination of Fe(III) with the BIPY method was carried out after the reduction of Fe(III) to Fe(II) with ascorbic acid and the Fe total was determined. The agreement for Fe(III) was quite good for the spectrophotometric methods (DPKSH and BIPY) for samples A (34%) and

Table 4. Comparison Between Fe^{n+} Concentrations in the Samples Using the DPKSH, BIPY, and AA Methods. Equations 3 and 5 (Table 2) Were Used to Calculate the Fe^{n+} Concentrations When the DPKSH Method Was Applied

Ion	Sample	A*	B*	C*	D*
Fe(II)	DPKSH(μM)	19.9	n.d	38.8	n.d
	BIPY(μM)	17.7	n.d	38.9	n.d
	E(%)	12	–	−0.3	–
Fe(III)	DPKSH(μM)	99.0	23.5	41.3	12.4
	BIPY(μM)	73.6	6.00	57.9	1.76
	E(%)	34	292	−29	604
Fe(II+III)	DPKSH(μM)	119	23.5	80.1	12.4
	BIPY(μM)	91.3	6.00	96.8	1.76
	E(%)	30	292	−17	604
	AA	94.9	5.37	66.2	n.d
	E(%)	25	338	21	–

n.d = not detected.
*The absorbance (A^{375}/A^{644}) ratios for the samples are: A (9.2); B (−); C (3.7) and D (−) and the Fe (III)/Fe(II) ratios are: A (4.9); B (−); C (1.1) and D (−).

Table 5. Comparison Between Fe(II + III) Concentrations Using DPKSH (Before and After Ascorbic Acid Reduction), BIPY, and AA Methods

	DPKSH					
Sample	Before	After	BIPY	E (%)	AA	E (%)
Am.B	23.5	6.80	6.00	13	5.35	27
Am.D	12.4	1.17	1.76	− 34	–	–

C (–29%) but not acceptable for samples B (292%) and D (604%), most likely due to the interfering absorbance of other possible cations present in the samples, which are coordinated by the reagent DPKSH and absorb at 375 nm, leading to positive errors in samples A, B and D. The negative error found for sample C is probably inherent to the BIPY method. Metallic ions like copper, nickel and zinc are the principal interferents (26) and may lead to a higher concentration of iron.

The comparison between the results from DPKSH and BIPY methods with respect to the Fe(II + III) concentration are shown in Table 4. These results show approximately the same relative errors as for Fe(III), and the same is true when we compare the results from DPKSH and AA methods for samples A and B. However, for sample C a positive error (21%) was found because a lower concentration of total Fe was detected using AA, probably due to chloride interference, causing losses from volatilization. For sample D no comparison may be done because total Fe was not detected using AA.

The comparison of all results (Table 4) confirms that the only interference in the DPKSH method occurs at 375 nm and it is more severe when the Fe(III) concentration is much higher than the Fe(II) concentration; such a case was found in samples B and D. This interference was suppressed carrying out the previous reduction of Fe(III) to Fe(II) with ascorbic acid like the BIPY method and measuring the absorbance at 644 nm. Table 5 shows the results for samples B and D. As can be seen the results are quite similar for sample B (DPKSH, BIPY and AA methods) and D (DPKSH and BIPY methods).

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